

# Relative Solubilities of Bifenox and 1-Naphthylacetic Acid (NAA) in Plant Cuticles and in Selected Pure or Aqueous Glycol Additives

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(Received 21 August 1997; revised version received 26 January 1998; accepted 4 March 1998)

**Abstract:** The driving force for foliar penetration is the product of the partition coefficient ( $K$ ) between the cuticle and the formulation residue, and the concentration of the active ingredient in the spray residue. Ethylene glycols and polyethylene glycols (PEGs) are often contained in commercial formulations, because they are good solvents and not toxic. Since they are humectants, the water content of the formulation residue varies with humidity of the air. At 25°C and 65% relative humidity PEG 400 contains about 50% water. The partition coefficients for the lipophilic herbicide, bifenox, increased with increasing water content of the ethylene glycols and PEGs, such that  $\log K$  was a linear function of the mass fraction of water or PEG. The  $K$  value was about 0.5 for the system cuticle/pure PEG and 27 500 for the system cuticle/water. When PEG contained 50% water,  $K$  was only 110. Partition coefficients of bifenox between cuticle and 'Tween' 80 depended also on humidity, having values of 0.75 in cuticle/pure 'Tween' 80 and 29.1 when 'Tween' 80 contained 50% water. With 1-naphthylacetic acid (NAA), which is a weak acid, partition coefficients also depended on water content of PEG 400, but a maximum curve was obtained. The maximum partition coefficient (211) was observed with a mixture of 30% PEG 400 and 70% water, which corresponded to a humidity of 88%. We suggest that this is due to an effect of PEG 400 on the ionisation of NAA. Our data demonstrate that partition coefficients are affected by humidity, because solubilities of lipophilic compounds and weak acids in PEG/water mixtures vary greatly with the water content. This in turn affects driving forces, mainly by the effect of humidity on partition coefficient. With non-ionisable lipophilic compounds, partition coefficients, driving forces and rates of foliar uptake therefore increase with increasing humidity. © 1998 SCI

*Pestic. Sci.*, **53**, 278–284 (1998)

Key words: bifenox; foliar penetration; humectants; NAA; partition coefficient; polyethylene glycol

## 1 INTRODUCTION

Commercial plant protection agents are usually formulated to aid solubility, wetting, handling and to optimise

biological activity. In addition to numerous surfactants, various glycols are sometimes used as adjuvants. Surfactants serve as wetting agents, emulsifiers and as accelerators. Accelerators are additives which increase rates of foliar uptake by increasing solute mobilities in cuticles.<sup>1–3</sup> Glycols and polyethylene glycols (PEGs) serve as solvents, antifreezers, and humectants, having low toxicity.<sup>4–6</sup> Due to their negligible penetration<sup>3,7–9</sup>

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Contract/grant sponsor: Deutscher Akademischer Austauschdienst.

they are not accelerators and thus influence rates of foliar uptake mainly by affecting driving forces.<sup>2,10–12</sup>

For foliar uptake, the driving force is the product of the partition coefficient (*K*) and the concentration (*C*) of the active ingredient. In most cases, plant-protection agents are applied to foliage in aqueous systems and the water evaporates quickly. Active ingredients and additives which do not penetrate into the cuticle during droplet drying form a mixed residue on the outer surface of the cuticle. For maximum rates of penetration this residue should be a saturated solution of the active ingredient in the additives.<sup>3,10,12</sup> Depending on the hygroscopicity of the active ingredients and additives, and the humidity of the surrounding air, the spray residue will contain various amounts of water. The solubility of the active ingredient in the additive residue is greatly affected by the water content of the additive residue, for instance when polyethylene glycols form a large fraction of the additive residue.<sup>11</sup> Thus, moisture affects driving forces by its effect on the solubility of the active ingredient in the additive residue, and its volume. As a consequence, rates of foliar uptake may be affected by the humidity of the air and this is frequently observed.<sup>13,14</sup>

Solubilities of active ingredient in hydrated residues of surfactants and ethylene glycols relative to the solubility in the cuticle have rarely been published, despite being of paramount importance with regard to rates of foliar penetration. Only recently have the partition coefficients cuticle/glycerol and cuticle/PEG 400 for seven organic compounds differing in octanol/water partition coefficient by six orders of magnitude been published and it was shown that the water content of polyethylene glycol (PEG 400) greatly affects partition coefficients.<sup>11</sup> Since ethylene glycols and PEGs of different molecular weights are used in formulations, we have studied the effect of molecular weight of ethylene glycols and poly-

ethylene glycols on partition coefficients of two actives. The very lipophilic bifenox and the moderately lipophilic and ionisable 1-naphthylacetic acid (NAA) were used as model compounds.

## 2 MATERIALS AND METHODS

### 2.1 Plant material

Cuticle/water partition coefficients of organic solutes do not vary much among plant species<sup>15</sup> and we have used only the fruit cuticles from green pepper fruits (*Capsicum annuum* L. cv. Bell Boy) and the upper cuticles from pear (*Pyrus communis* L. cv. Bartlett) leaves in our experiments. The cuticles were isolated enzymatically,<sup>16</sup> air-dried and stored at 8°C. Prior to use they were cut into small pieces and they will be referred to as cuticular membranes (CM).

### 2.2 Chemicals

[*U*-<sup>14</sup>C]Bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate) having a specific activity of 1288 MBq mmol<sup>-1</sup> and a radiochemical purity of 99.6%, was obtained from International Isotopes, München, Germany. [*Carboxyl*-<sup>14</sup>C] NAA was obtained from Sigma Chemie, Deisenhofen, Germany. It had a specific activity of 85 MBq mmol<sup>-1</sup> and a radiochemical purity of 98%. Other non-labelled chemicals used are listed in Table 1. PEGs had a low water content (<0.5%) and were stored over silica gel in a desiccator before use.

TABLE 1  
Common and Chemical Names, Molecular Weight, Melting Point and Sources of Additives

Common name <sup>a</sup>	Chemical name	Relative molecular mass	Melting point (°C)
Glycerol	1,2,3-Propanetriol	92.1	18.2
Ethylene glycol <sup>1</sup>	1,2-Ethanediol	62.1	-12
Diethylene glycol <sup>1</sup>	2,2'-Oxybis-ethanol	106.1	-6
Triethylene glycol <sup>1</sup>	2,2'-[1,2-Ethanediyl-bis(oxy)]bis-ethanol	150.7	-7
Tetraethylene glycol <sup>1</sup>	2,2'-[Oxybis(2,1-ethanediyl-oxy)]bis-ethanol	194.2	-5
Polyethylene glycol 200 <sup>2</sup>	$\alpha$ -Hydro- $\omega$ -hydroxypoly(oxy-1,2-ethane)	190–210 <sup>b</sup>	-37
Polyethylene glycol 400 <sup>3</sup>	$\alpha$ -Hydro- $\omega$ -hydroxypoly(oxy-1,2-ethane)	380–420 <sup>b</sup>	1–5
Polyethylene glycol 600 <sup>1</sup>	$\alpha$ -Hydro- $\omega$ -hydroxypoly(oxy-1,2-ethane)	570–630 <sup>b</sup>	17–23
Pluronic 101 <sup>2, c</sup>	—	—	—
'Tween' 80 <sup>3</sup>	Polyoxyethylene (20) sorbitan monooleate	—	—

<sup>a</sup> 1 = Fluka Chemie, Buchs Switzerland, 2 = Serva Heidelberg/New York, 3 = Merck Schuchardt, Hohenbrunn Germany.

<sup>b</sup> Average molecular masses given by the manufacturer.

<sup>c</sup> 9 : 1 mixture of polypropylene glycol and polyethylene glycol.

### 2.3 Partition coefficients

Partition coefficients between cuticle and aqueous solutions or liquids were determined as described in detail by Baur *et al.*<sup>11</sup>  $K_{\text{CM/L}}$  as defined by eqn (1) is the ratio of the equilibrium concentrations of a solute in the CM ( $C_{\text{CM}}$ ) and the adjacent liquid or solution ( $C_{\text{L}}$ ):

$$K_{\text{CM/L}} = \frac{C_{\text{CM}}}{C_{\text{L}}} = \frac{M_{\text{CM}}/m_{\text{CM}}}{M_{\text{L}}/m_{\text{L}}} \quad (1)$$

$C_{\text{CM}}$  was calculated from the amounts ( $M$ ) of radioactivity and the masses ( $m$ ) of the CM and the liquid, respectively. Thus, partition coefficients were calculated using molal concentrations, which do not depend on temperature. The masses of the CM ( $m_{\text{CM}}$ ) varied between 1 and 5 mg (depending on estimated partition coefficients) and were measured using a microbalance ( $\pm 1 \mu\text{g}$ , Sartorius, Göttingen, Germany). The liquid mass ( $m_{\text{L}}$ ) was 1 g. CM and the liquids (containing the radiolabelled model compounds at 600 to 2000 Bq) were placed in small glass vials with Teflon-lined screw caps (Wheaton, Millville, USA) and mixed on a roller bench ( $40 \text{ rev min}^{-1}$ ) until sorption equilibrium was obtained (24 to 48 h). Most experiments were carried out at ambient temperatures ( $23\text{--}25^\circ\text{C}$ ). When temperature was an experimental variable, the roller bench was placed in a controlled temperature cabinet with  $\pm 0.5^\circ\text{C}$  precision. In the experiment with bifenoxy and 'Tween' 80, the CM were first loaded with bifenoxy from aqueous solutions, air-dried and then equilibrated with the test solutions. Mass fractions of PEGs and water of 1.0, 0.7, 0.5, 0.3 and zero were used.

When equilibrium had been obtained, CM pieces were removed from the liquids, blotted dry with soft tissue paper and weighed. This wet weight was often

significantly higher than the dry weight determined initially, since CM sorb up to 10% water<sup>17</sup> and aqueous solutions of PEGs and liquid adhered to the surface. From the difference in weight of dry CM and the CM with adhering liquid, the radioactivity not associated with the cuticle could be calculated. In those cases where the radioactivity associated with this adhering liquid was substantial ( $> 5\%$  of the radioactivity in the CM), it was subtracted from the total radioactivity of the CM. This correction was necessary when partition coefficients were low, so that the radioactivity in CM was low, while it was high in the surrounding liquid phase.<sup>11</sup> After weighing, CM were placed in scintillation cocktail (Aquasafe 500, Zinsser Analytic, Frankfurt am Main, Germany) to first extract the radioactive model compounds from the CM prior to assaying them for radioactivity. (Packard CA 2000 scintillation counter, Downers Grove, IL, USA). From the liquids two aliquots were taken and their radioactivities determined. Experiments were replicated five to 15 times, and the counting error ( $2\sigma$ ) was 2%. Arithmetic means and 95% confidence intervals are reported.

### 3 RESULTS

In the range 15 to  $35^\circ\text{C}$ , temperature did not significantly affect partition coefficients for the system pear CM and PEG 400. With pure PEG 400, partition coefficients of bifenoxy were  $0.88(\pm 0.08)$  at  $15^\circ\text{C}$ ,  $0.72(\pm 0.20)$  at  $25^\circ\text{C}$  and  $0.88(\pm 0.12)$  at  $35^\circ\text{C}$ . With aqueous PEG 400 (mass fraction 0.5), partition coefficients were higher by a factor of 150, but, again, there was no significant temperature effect.

Bifenoxy is highly lipophilic, as borne out by a cuticle/water partition coefficient of 27 500 (Table 2). The solubility of bifenoxy in glycerol and ethylene glycol was

TABLE 2  
Partition Coefficients ( $K_{\text{CM/L}}$ ) for Bifenoxy between Pepper Fruit Cuticle and Selected Liquid Additives in Different Mixtures with Water

Compound	1.0	$K_{\text{CM/L}}^a$ Mass fraction of compound		$K(0.5)/K(1.0)$
		0.7	0.5	
Water <sup>b</sup>	27 500 ( $\pm 2200$ )	—	—	—
Glycerol <sup>b</sup>	200 ( $\pm 52$ )	—	—	—
Ethylene glycol	6.89 ( $\pm 0.31$ )	184 ( $\pm 117$ )	494 ( $\pm 117$ )	72
Diethylene glycol	0.75 ( $\pm 0.06$ )	—	166 ( $\pm 72.6$ )	221
Triethylene glycol	0.82 ( $\pm 0.05$ )	—	201 ( $\pm 45.8$ )	245
Tetraethylene glycol	0.73 ( $\pm 0.09$ )	—	108 ( $\pm 32.8$ )	148
'Pluronic' 101	0.61 ( $\pm 0.05$ )	—	—	—
'Tween' 80	0.75 ( $\pm 0.16$ )	13.2 ( $\pm 4.5$ )	29.1 ( $\pm 3.7$ )	39

<sup>a</sup> Arithmetic means of 7 to 15 determinations with 95% confidence intervals.

<sup>b</sup> Data taken from Baur *et al.*, Reference 11.

much higher than in water but, since  $K > 1$ , solubility in the cuticle was still higher than in the two liquids. The other glycols listed in Table 2 were better solvents for bifenox than the pepper fruit cuticle and increasing molecular weights of ethylene glycols had no significant effect on partition coefficients for the systems CM/pure liquids. The surfactants 'Tween' 80 and 'Pluronic' 101 had partition coefficients comparable to the higher molecular weight glycols. Diluting glycols and surfactants with water increased partition coefficients, but the effect of dilution was not the same for all compounds (Table 2, last column). With increasing molecular weight of glycols, the ratio of the partition coefficients, measured at a mass fraction of 0.5, over that measured using pure glycols increased from 72 to 245. With 'Tween' 80, the increase in  $K$  due to dilu-

tion with water (mass fraction 0.5) was only 39-fold. 'Pluronic' 101 formed a gel with 50% water, which prevented us from accurately determining partition coefficients.

For the systems CM/PEG 200, CM/PEG 400 and CM/PEG 600, the logarithms of the partition coefficients increased linearly when the PEGs were diluted with water (Fig. 1). The y-intercepts (mass fraction of PEG, zero) give the CM/water partition coefficient for pepper CM and bifenox as  $3.31 \times 10^4$ . The slopes of the three graphs do not differ significantly, the average slope being 4.96; for pure PEGs an average partition coefficient of 0.49 can be calculated.

In contrast to the data obtained with bifenox, partition coefficients measured for NAA using the system pepper CM/ aqueous PEG 400 showed an optimum

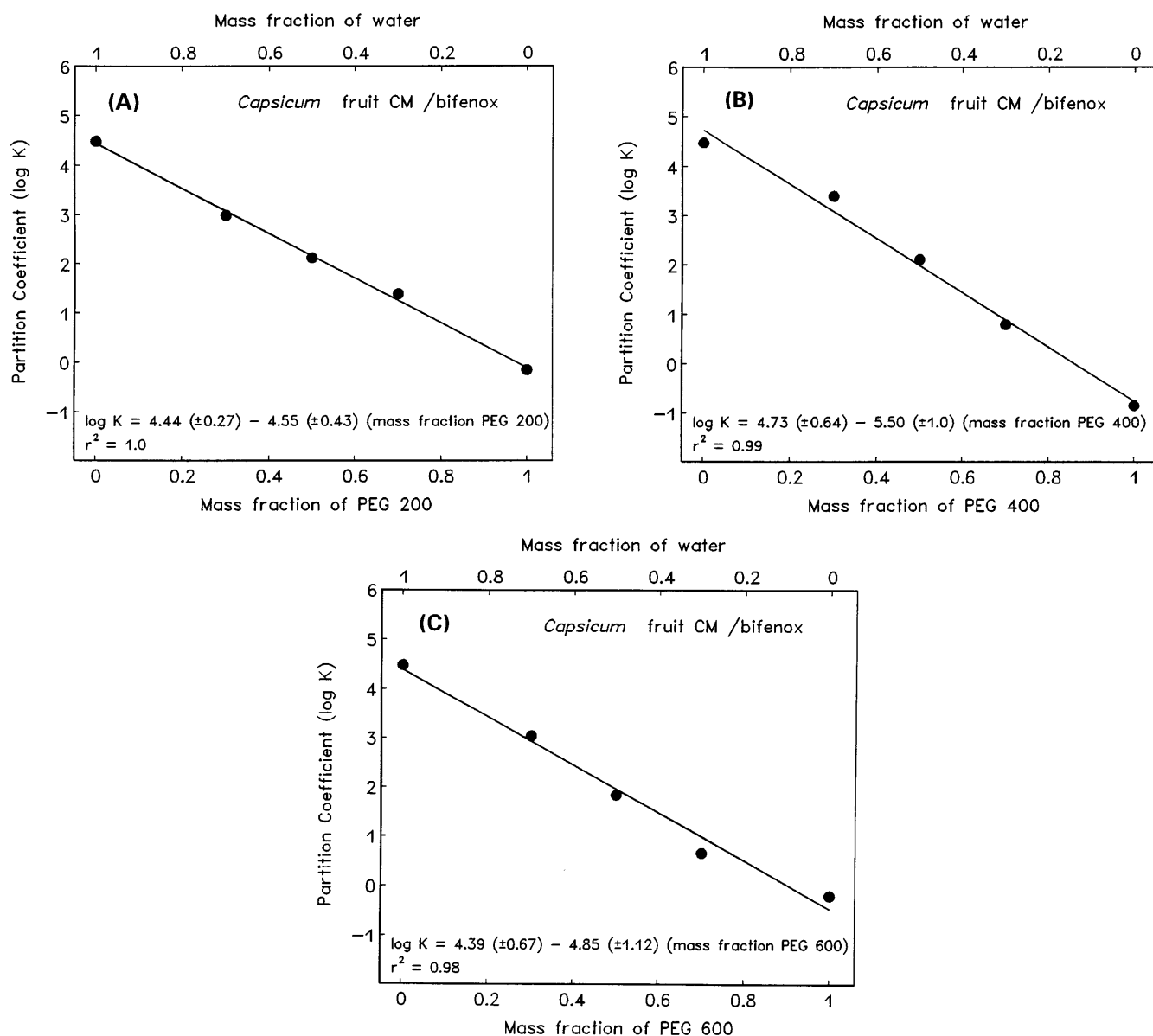


Fig. 1. Partition coefficients of bifenox between green pepper fruit cuticles and PEG/water mixtures as affected by mass fractions of (A) PEG 200, (B) PEG 400 and (C) PEG 600.

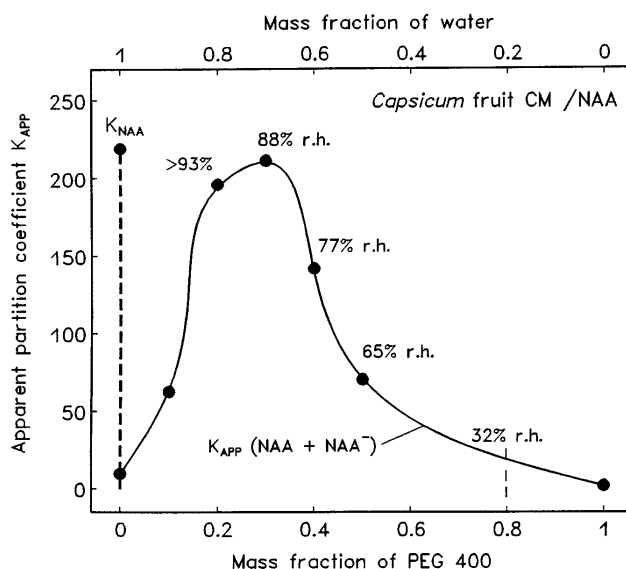


Fig. 2. Dependence of partition coefficients for NAA and green pepper fruit cuticles on mass fraction of aqueous PEG 400 (arithmetic means of 8–10 replications, standard error <20%).  $K_{NAA}$  is the partition coefficient of the non-ionised acid. The relative humidities which result in the respective mass fractions of PEG 400 in water are given adjacent to the data points.

curve having a maximum at a mass fraction of PEG 400 of 0.3 (Fig. 2). At higher or lower dilution with water, partition coefficients decreased rapidly and reached 9.8 in pure distilled water in equilibrium with carbon dioxide of the air (pH 5.5) and 1.8 in pure PEG 400.

#### 4 DISCUSSION

Rates of uptake of active ingredients ( $J$ ,  $\text{mol m}^{-2} \text{s}^{-1}$ ) into leaves are proportional to the solute mobility in the cuticle ( $k^*$ ,  $\text{s}^{-1}$ ) and the driving force. When active ingredients do not accumulate in the epidermal cell wall once they have penetrated the cuticles, a simple equation can describe steady-state rates:<sup>12</sup>

$$J = k^* l_{ls} (K_{CM/fr} C_{fr}) \quad (2)$$

In eqn (2),  $l_{ls}$  is the thickness of the limiting skin of the cuticles,<sup>2,12</sup> which is of the order of 0.2 to  $1 \times 10^{-6}$  m,  $K_{CM/fr}$  is the partition coefficient between the CM and the formulation residue in equilibrium with the moisture of the surrounding air, and  $C_{fr}$  is the concentration of the active ingredient in the formulation residue. The term in parentheses is the driving force of penetration. Both quantities can vary independently, and, for maximum rates of penetration, the product should be as large as possible.

The rate of penetration is also proportional to the solute mobility in the cuticles ( $k^*$ ) and depends on plant species, size of active ingredients, temperature and, for some active ingredients, also on concentration.<sup>10,12,18</sup> Solute mobilities can be greatly increased by acceler-

ators which increase the fluidity of cuticular waxes.<sup>12</sup> Many additives are accelerators<sup>1–3</sup> but glycerol and the glycols studied here are not.<sup>3,11,19</sup> Thus, glycols and PEGs can influence rates of foliar uptake only by affecting partition coefficients and/or concentrations in the residue.

The glycols and the other adjuvants we studied are hygroscopic, the water content of the formulation residue increasing with humidity. In the humidity range 11–93%, the water content of PEG 400 increased in a linear fashion<sup>11</sup> and, using the equation

$$\% \text{ mass PEG 400} = 109 - (0.9 \times \text{R.H.})$$

it can be calculated that, at 30% humidity, PEG 400 contains 18% water, at 50%, 36% water and at 80% humidity, 63% water. Humidities in this range occur frequently in the field and, since we have shown that water content of glycols, PEGs and 'Tween' 80 greatly affects partition coefficients, we can examine the implications for foliar uptake of plant protection agents.

Firstly, we observed that temperatures between 15 and 35°C had no significant effect on partition coefficients, which implies that the results obtained at 23–25°C can be applied to lower and higher temperatures. Partition coefficients increased with increasing water content of all liquid adjuvants tested (Table 2) and, with the three PEGs, it was shown that this dependence was linear and could be predicted using simple linear equations (Fig. 1). Neither y-intercepts nor slopes differed significantly for the three PEGs and a common equation valid for all PEGs could be obtained by averaging the parameters:

$$\log K_{CM/Liquid} = 4.52(\pm 0.25) - 4.96(\pm 0.42) \times \text{mass fraction of PEG} \quad (3)$$

From the y-intercept, a CM/water partition coefficient of 33 100 can be calculated, which is close to the value of 27 500 obtained earlier by direct determination.<sup>11</sup> The other extreme is the partition coefficient CM/pure PEG of 0.49. Neither value is of practical significance, since formulations always contain adjuvants and 0% humidity needed to form a pure PEG residue on the leaf surface does not occur in the field or the greenhouse. However, it is interesting to note that the partition coefficient obtained with pure PEG is close to the average measured with the glycols (except ethylene glycol), 'Pluronic' 101 and 'Tween' 80. All of these additives have the same solvent power for the lipophilic bifenoxy. Since the partition coefficient is smaller than unity, this indicates that bifenoxy is somewhat more soluble in these adjuvants than in the cuticular membrane. This is not desirable because it makes the driving force (eqn (2)) very small. Fortunately, partition coefficients and driving forces increase with humidity and, at 50% relative humidity, they were 39 to 245 times larger

with the compounds listed in Table 2. For the PEGs, partition coefficients at 50% humidity would be 110, which is about 220 times larger than with pure PEGs; it follows from eqn (2) that rates of foliar penetration increase by the same factor.

The beneficial effect of high humidities, as far as partition coefficients and driving forces are concerned, is somewhat counteracted by a dilution effect. For instance, PEG 400 contains about 36% water at 50% humidity. This increases the total volume of the residue by 36% and the concentration in the residue ( $C_r$ ) decreases by about 32%. This is a small effect relative to the increase in partition coefficients. Furthermore, the total volume after mixing is often smaller than the sum of the volumes of the liquids mixed.

NAA is a lipophilic compound, but it showed a different response to water content of PEG 400 (Fig. 2). The partition coefficient had a maximum value of 211 at a water content of 70%, while in pure water the partition coefficient was 9.8. However, a CM/water partition coefficient for pepper fruit CM and NAA of 220 has been reported.<sup>20</sup> This value was determined using buffered solutions and calculation was based on the concentration of non-ionised NAA. Ionised NAA is not lipophilic and has a partition coefficient  $<1$ . An apparent partition coefficient of 9.8 was determined with distilled water in equilibrium with carbon dioxide of the air (pH 5.5). This apparent partition coefficient was calculated using the total NAA concentration rather than the concentration of the non-ionised species. At pH 5.5, only 4.77% of the NAA molecules are ionised, since the  $pK_a$  is 4.2.<sup>21</sup> Correcting for the degree of ionisation, a partition coefficient of 205 is obtained ( $9.8/0.0477$ ), which is very close to the published value of 220 (Fig. 2). Apparent partition coefficients measured with aqueous PEG 400 solutions varied with water content, but most were smaller than the true partition coefficient of 220. Only at a mass fraction of water of 0.7 was the apparent partition coefficient close to the one determined for non-ionised NAA; one might speculate that under this condition 96% of the NAA was not ionised ( $211/220 \times 100$ ). Ionisation of NAA varied, depending on the mass fraction of PEG 400. The reduction of the ionised fraction might be caused by change in the dielectric constant, which is lower, e.g. for pure tetraethylene glycol ( $\epsilon = 20.4$ , 20°C), than for water ( $\epsilon = 80.1$ ). However, we have no values for pure PEGs or mixtures with water. Nevertheless, it is an interesting observation that, with unbuffered formulations, high partition coefficients and high driving forces can be obtained with PEGs having the appropriate water content. Since this depends on relative humidity, the degree of ionisation and apparent partition coefficient vary with humidity (Fig. 2). Thus, rates of penetration of weak acids (and possibly weak bases) will depend on humidity, if the formulation contains enough ethylene glycols or PEGs. Again, this is an effect of humidity on driving forces

(eqn (2)). The partition coefficient for NAA with pure PEG 400 is about 4-fold higher than that obtained for bifenoX, indicating that the solubility of the more lipophilic bifenoX is better in PEGs.

Having shown that humidity has a very large effect on driving forces because it affects the water content of PEGs and partition coefficients, we can now consider the second determinant,  $C_{fr}$ . For maximum rates of uptake, this quantity should also be as large as possible. If the formulation is simply a saturated solution of PEGs, problems with very lipophilic active ingredients will arise if water is used as carrier. The actives will precipitate and this must be prevented by including an emulsifier. If the formulation is a suspension of fine particles of the active material in PEGs and other additives, the PEGs will serve as solvents and as liquid interface between the particles and the cuticle. In this situation, both partition coefficients and  $C_{fr}$  will be affected by humidity as described above.

These arguments are valid only for lipophilic active ingredients, because with very polar compounds ( $K_{cw} < 1$ ), cuticle/water partition coefficients and cuticle/PEG partition coefficients are similar, being smaller than unity; humidity and water content of PEG/s will have little effect. For instance, for methylglucose the partition coefficients cuticle/water or cuticle/pure PEG 400 are 0.13 and 0.4, respectively<sup>11</sup> and precipitation on dilution with water will be no problem. The extent to which humidity affects the penetration of polar active ingredients in the presence of PEGs is currently being investigated.

## ACKNOWLEDGEMENT

We thank the DAAD (Deutscher Akademischer Austauschdienst) for financial assistance to one of us (H.M.).

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